

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 23-05-2006		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE  A New Silicon-Containing Bis(Cyanate) Ester Resin with Improved Thermal Oxidation and Moisture Resistance (Preprint)				5a. CONTRACT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Andrew J. Guenther, Gregory R. Yandek, Michael E. Wright, Brian J. Petteys, Roxanne Quintana, & Dan Connor (NAVAIR); Richard D. Gilardi (Naval Research Laboratory); Darrell Marchant (AFRL/PRSM)				5d. PROJECT NUMBER 23030521	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/PRSM 9 Antares Road Edwards AFB CA 93524-7401				8. PERFORMING ORGANIZATION REPORT NUMBER  AFRL-PR-ED-JA-2006-178	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/PRSM 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-JA-2006-178	
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited (AFRL-ERS-PAS-2006-132)					
13. SUPPLEMENTARY NOTES To be published in the ACS journal Macromolecules.					
14. Abstract  A new cyanate ester monomer was prepared from bis(4-cyanatophenyl)-dimethylsilane (SiMCy) and fully characterized by analytical and spectroscopic techniques. The monomer was found to have a melting point about 20 °C lower than that of the commercial bis(4-cyanatophenyl)dimethylmethane (BADCy) with similar melt viscosity, curing kinetics, and post-cure glass transition temperature. Analysis of the single-crystal molecular structure by x-ray diffraction showed that intermolecular packing was dominated by weak hydrogen-bonding attractions between the aromatic rings and the –OCN nitrogen atoms. In contrast, the packing interactions found in BADCy are dominated by dipole-dipole interactions of the OCN groups. These differences may explain the 50% reduction in moisture uptake observed in SiMCy as compared to BADCy during exposure to boiling water. In addition, thermogravimetric analysis revealed that SiMCy exhibited a significantly higher char yield in air than BADCy, presumably due to the formation of silicates at high temperature. The combination of improved thermo-oxidative stability and reduced moisture absorption without significant loss in ease of processing or mechanical properties makes SiMCy an important potential “drop in” replacement for BADCy, and demonstrates the power of the molecular level approach to designing new high-temperature polymer materials.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  SAR	18. NUMBER OF PAGES  35	19a. NAME OF RESPONSIBLE PERSON Dr. Joseph Mabry
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A

# A New Silicon-Containing Bis(Cyanate) Ester Resin with Improved Thermal Oxidation and Moisture Resistance (Preprint)

Andrew J. Guenthner<sup>†\*</sup>, Gregory R. Yandek<sup>†</sup>, Michael E. Wright<sup>†\*</sup>,  
Brian J. Petteys<sup>†</sup>, Roxanne Quintana<sup>†</sup>, Dan Connor<sup>†</sup>, Richard D. Gilardi<sup>††</sup>, and Darrell  
Marchant<sup>†††</sup>

<sup>†</sup>NAVAIR, Research & Engineering Sciences, Research Department,  
Chemistry Division, China Lake, California 93555

<sup>††</sup>Laboratory for Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375

<sup>†††</sup>Air Force Research Laboratory, Propulsion Materials Application Branch,  
Edwards AFB, CA 93524

E-mail: andrew.guenthner@navy.mil

**Keywords:** cyanate ester; thermosetting resins; cure kinetics; thermal stability, silicon, moisture uptake, mechanical properties, molecular structure

**Abstract.** A new cyanate ester monomer was prepared from *bis*(4-cyanatophenyl)-dimethylsilane (SiMCy) and fully characterized by analytical and spectroscopic techniques. The monomer was found to have a melting point about 20 °C lower than that of the commercial *bis*(4-cyanatophenyl)dimethylmethane (BADCy) with similar melt viscosity, curing kinetics, and post-cure glass transition temperature. Analysis of the single-crystal molecular structure by x-ray diffraction showed that intermolecular packing was dominated by weak hydrogen-bonding attractions between the aromatic rings and the –OCN nitrogen atoms. In contrast, the packing interactions found in BADCy are dominated by dipole-dipole interactions of the OCN groups. These differences may explain the 50% reduction in moisture uptake observed in SiMCy as compared to BADCy during exposure to boiling water. In addition, thermogravimetric analysis revealed that SiMCy exhibited a significantly higher char yield in air than BADCy, presumably due to the formation of silicates at high temperature. The combination of improved thermo-oxidative stability and reduced moisture absorption without significant loss in ease of processing

or mechanical properties makes SiMCy an important potential “drop in” replacement for BADCy, and demonstrates the power of the molecular level approach to designing new high-temperature polymer materials.

## Introduction

Cyanate ester resin systems have recently attracted increasing attention as next-generation thermosetting polymer matrices for continuous fiber reinforced composites due to their outstanding resistance to fire and moisture, combined with good strength at elevated temperatures, and compatibility with carbon fiber reinforcements.<sup>1</sup> Although polycyanurates or triazines (i.e. the thermoset network that results from trimerization of the bis(cyanate) monomers) can exhibit improved mechanical toughness in comparison to other thermosetting polymers, significant improvements in fracture resistance are still needed for many applications.<sup>2-3</sup> Effective toughness enhancement in polycyanurate systems has been realized through the incorporation of thermoplastic additives<sup>4-11</sup> that can withstand higher temperatures than elastomeric species. However, attempts to toughen cyanate ester resins using various thermoplastics have almost always adversely affected one or more key physical properties.<sup>12-23</sup>

Fortunately, some very recent developments have now made more systematic investigations of cyanate esters significantly more feasible. One such development is the availability of a wide variety of agents capable of being dispersed at the nanometer scale in thermosetting resin systems. These include everything from polyhedral oligomeric silsesquioxane (POSS),<sup>23-25</sup> at around 1 nm, through functionalized nanoclay particles at 1 x 100 x 100 nm,<sup>26-28</sup> to more traditional additives and thermoplastic tougheners on the scale of microns. Another development, which will be further explored herein, is the creation of new synthetic routes to cyanate esters that allow enormous diversity in the structure of the starting material, essentially allowing the structure to be tailored at the molecular level. When combined with the developments in nanotechnology and systematic examination of more traditional elastomeric and

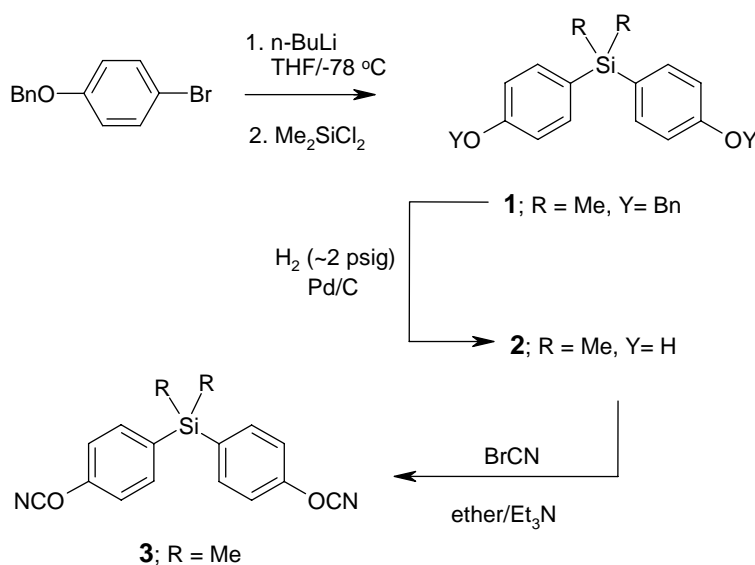
thermoplastic tougheners, the availability of these new atomically-tuned cyanate esters thus serves as the cornerstone in the systematic design of improved polycyanurate systems.

The key physical properties that serve as a basis for identifying “improved” polycyanurate systems include 1) ease of processing, 2) glass transition temperatures (generally in the range of 200 – 300 °C), 3) mechanical properties such as elastic modulus and impact strength, 4) thermo-oxidative stability, and 5) moisture absorption. Since the incorporation of silicon at a molecular level has recently been shown to impart improvements in mechanical properties, flame-retardance, and char yields in cured epoxy resins,<sup>29,30</sup> the insertion of silicon (at the molecular level) into the monomer connecting structures of cyanate esters seems a logical starting point for tailoring the molecular structure to achieve improved physical properties. In this paper we will describe how a new silane-based synthetic method for producing cyanate ester resins has been exploited to produce a superior polycyanurate material. We will demonstrate the flexibility of this technique by describing its use in preparing a cyanate ester that differs from commercially available materials by the replacement of a single carbon atom with a silicon atom in the monomer, yet shows significant improvements in thermo-oxidative and moisture resistance. Thus, in essence, we will explore the effect of silicon incorporation at the smallest possible length scale. The result will therefore provide a unique point of comparison to materials modified at the nanoscale. Moreover, modification at this scale is far less likely to result in substantial increases in monomer viscosity, thus preserving the relatively easy processing that makes cyanate esters attractive. By showing that it is possible to obtain significantly improved properties by the change of a single atom, the results presented herein demonstrate the power of a systematic molecular level approach to develop new high performance polymer composite resins with greatly improved physical properties for use across a wide variety of applications.

## Results and Discussion

**Synthesis and purification of bis(4-cyanatophenyl)dimethylsilane.** The synthetic route for production of *bis*(4-cyanatophenyl)dimethylsilane (**3**) is shown in Scheme 1.<sup>31</sup> Because the starting materials are dichlorodialkylsilanes, a wide variety of chemical structures may be produced using the same reaction sequence. However, monomer **3** (SiMCy) has been singled out for study largely because the commercially available bisphenol-A dicyanate ester monomer, referred to as BADCy, is analogous in that it differs from SiMCy only by the presence of one *sp*<sup>3</sup>-carbon in place of the silicon. BADCy has been commercially available for over four decades and is extremely well characterized,<sup>1</sup> making it an ideal comparative material.

**Scheme 1**



Because the chemical reactivity of cyanate ester resins may be greatly affected by even small levels of impurities, especially with the presence of phenols, it is important to understand the nature of any impurities present in the sample.<sup>1</sup> A sensitive indicator of the presence of performance-altering impurities in cyanate ester resins is the melting endotherm observed via differential scanning calorimetry (DSC),<sup>33</sup> which is shown in Figure 1 for SiMCy and BADCy over the temperature range of 45 to 100 °C. Generally speaking, increasing levels of impurities broaden and shift crystal melting endotherms to lower temperatures, with impurity levels as low as 2% leading to major changes in peak shape. As evident from the peak shapes, the observed levels of impurities are similar in both materials, although the melting point of SiMCy is about 20 °C lower than that of BADCy. In addition, the comparative difference in melting points between the two compounds is likely not explained by effects caused by impurities since according to the literature, a 7.2 mole % level of impurity results only in a 6.6 °C reduction in the peak melting temperature for BADCy.<sup>1</sup>

\*\*\*\*\* *Insert Figure 1 here* \*\*\*\*\*

In addition, an analysis via HPLC (shown in Figure 2) of SiMCy revealed impurities at level of around 3%. This compares to a level of around 2% in a sample of the commercial compound BADCy supplied by Lonza. The difference results from the detection of two additional low-level impurities in the sample of SiMCy, otherwise the distribution of impurities appears identical. Since commercial cyanate ester materials will always contain some impurities, the properties of the completely pure monomers (which may not even cure) are of limited practical significance. Nonetheless, it must be considered that comparisons between the two as-

received materials involve not only a difference in chemical structure of the main constituent but also a difference in the impurity set. Thus in each comparative case we have carefully examined and noted what role (if any) impurity set differences might play in shaping the results.

\*\*\*\*\* *Insert Figure 2 here* \*\*\*\*\*

**Chemical Reactivity.** Non-isothermal DSC scans of SiMCy and BADCy in the range of 100 to 350 °C are presented in Figure 3a, while the non-isothermal DSC scan of the polycyanurates cured according to the standard schedule for BADCy are shown in Figure 3b. Both the cyclotrimerization onset and exothermic peak temperatures are somewhat lower for SiMCy compared to BADCy. After curing, however, the glass transition temperature of cured SiMCy is only about 10 °C lower than that of cured BADCy. Since the presence of impurities is known to lower the curing temperature of cyanate esters by a considerable extent, the most likely explanation for the lower temperature cure of SiMCy is the slightly higher level of observed impurities, although the substitution of silicon for carbon may have an indirect effect by increasing the flexibility of the monomer somewhat. The slightly lower Tg of the cured system could also result from the substitution of more flexible carbon-silicon linkages in SiMCy.

\*\*\*\*\* *Insert Figure 3 here* \*\*\*\*\*

Another explanation for the difference in Tg between cured SiMCy and cured BADCy would be a difference in the extent of cure. Since such differences could also affect other properties, the use of a curing procedure that resulted in a high degree of cure with minimal



differences between materials was desired. Since SiMCy was observed to cure at lower temperatures than BADCy, it seemed reasonable that a process designed to achieve near complete cure in BADCy would do the same for SiMCy, thereby minimizing differences in the extent of cure between materials. Thus, we employed the following standard baking protocol designed to achieve near complete cure of BADCy: 100 °C for 30 min., followed by 150 °C for 30 min., 200 °C for 1 h, and lastly 250 °C for 3 h. A comparison of FTIR spectra between the uncured monomers in Figure 4(a) and the cured products in Figure 4(b) demonstrates that near-complete cyclotrimerization occurs. Comparison of the spectra show clearly that characteristic absorption bands of the cyanate ester functional groups (a triplet between 2200 and 2300  $\text{cm}^{-1}$ ) are replaced by absorbance bands corresponding to the triazine ring near 1370 and 1505  $\text{cm}^{-1}$  during cure.

The similarity in impurity profiles, the slightly lower melting cure, and glass transition temperatures, and the achievement of near complete cure using standard procedures for BADCy, when considered together, all strongly suggest that SiMCy could be employed as a “drop in” substitute for BADCy with only minor adjustments in processing required. Moreover, the viscosity of molten SiMCy was observed to be nearly identical to that of molten BADCy, while both BADCy and SiMCy could be cured at much lower temperature with the deliberate addition of catalysts at similar levels. Thus, as expected, substitution of silicon for carbon at the molecular level and at a site that is chemically remote from the reactive groups appears to alter the reactive chemistry and processing only in small and indirect ways, a feat that would be virtually impossible to achieve with substitution at the *micro*- or even *nano*- scale.

\*\*\*\*\* Insert Figure 4 here \*\*\*\*\*

**Single-crystal molecular x-ray structure determination.** As previously mentioned, the melting point of SiMCy differs from BADCy to a degree that is not readily explained by differences in purity, implying that a significant difference in solid-state structure between the two compounds exists. To probe the effect of substitution of silicon for carbon on the molecular structure and crystal packing, a single-crystal x-ray diffraction study on SiMCy has been completed.<sup>34</sup> Of particular interest to this study is the report on the corresponding structure and packing of BADCy, where a very complete analysis was presented.<sup>35</sup> X-ray quality crystals of **3a** were formed spontaneously during standing after removal of the solvent following isolation. A summary of selected data for the structure determination is presented in Table 1 and a drawing showing a single molecule is presented in Figure 5.

\*\*\*\*\* *Insert Figure 5 and Table 1 here* \*\*\*\*\*

The first of two electrostatic interactions found for the packing interactions in crystalline SiMCy is between the aromatic hydrogen C2B and the cyanate ester nitrogen atom (N3) (Figure 6). This occurs in what can be viewed as a dimer-like structure. The van der Waals (vdW) contact for N-H is approximately 2.65-2.75 Å, and so the calculated interaction of 2.84 Å is just slightly beyond that considered a formal hydrogen-bond.

\*\*\*\*\* *Insert Figure 6* \*\*\*\*\*

A second significant interaction is found between aromatic CH's (e.g. C3A) and again the cyanate ester nitrogen atoms (N3); however, this time the calculated distance of 2.62 Å is closer than the vdW distance and can thus be called a weak hydrogen-bond type of interaction (Figure 7). This interaction serves to connect the molecules in a continuous ribbon like array of molecules. Thus, although for BADCy in the molecular structure it is clear that dipole-dipole interactions for the cyanate ester groups dominate the crystal packing forces, it appears for SiMCy they do not.

\*\*\*\*\* *Insert Figure 7*\*\*\*\*\*

**Mechanical properties.** Table 2 shows the observed unnotched Izod impact strength (ASTM D 256), tensile modulus, elongation to failure (ASTM D 638), and coefficient of thermal expansion (40-100 °C) via thermomechanical analysis (TMA) of cured samples of SiMCy, compared to measured or reported values for BADCy. Due to the small batch size used for synthesis, the number of samples is limited to one or two per measurement, thus only qualitative comparisons can be made. According to the table, cured samples of SiMCy exhibit dry mechanical properties that are similar to those for BADCy, with a somewhat lower elastic modulus and higher thermal expansion coefficient likely for cured SiMCy. Given the physical and chemical similarities between the two compounds described previously, only small differences would be expected, including a somewhat lower elastic modulus and higher coefficient of thermal expansion due to the flexibility of the carbon-silicon linkages.

\*\*\*\*\* *Insert Table 2 here*\*\*\*\*\*

**Thermochemical stability.** Figures 8(a) and 8(b) show the weight loss and weight loss rate of cured SiMCy and cured BADCy when heated at 10 °C/min in both nitrogen (a) and in air (b). In nitrogen, cured SiMCy performs substantially worse than cured BADCy, with higher weight loss rates at temperatures from 410 °C to around 490 °C. The char yield at 600 °C is also reduced from 49% in cured BADCy to 43% in cured SiMCy. The decreased thermal stability might result from the substitution of carbon-silicon bonds for carbon-carbon in each repeating unit. Although impurities could also play a role in the difference in performance under nitrogen, the presence of a different set of impurities is very unlikely to explain the unusual difference between the performance in nitrogen and in air. As Figure 8(b) reveals, in air, cured SiMCy performs substantially better than cured BADCy, with the primary weight loss in cured BADCy around 450 °C transferred in part to higher temperatures, and the secondary weight loss above 520 °C curtailed almost entirely in cured SiMCy. As a result, the char yield at 600 °C is around 50% for cured SiMCy compared to 33% for cured BADCy. Other silicon containing polymers have shown similar improvements in thermo-oxidative stability in the past.<sup>36</sup> A possible explanation in the present case would be the formation of SiO<sub>2</sub> during the thermal decomposition of cured SiMCy. The silicon content of the monomer is fairly high at 9.5 wt-%. Since the fire resistance of cyanate ester resins is one of the main drivers for use in composite applications, the incorporation of silicon in SiMCy represents a favorable path for achieving improved fire resistance without altering the established processing procedures in cyanate ester resins.

\*\*\*\*\* *Insert Figures 8(a) and 8(b) here* \*\*\*\*\*

**Effects of moisture.** Figure 9 compares the weight gain recorded in cured samples of both SiMCy and BADCy exposed to boiling water for periods up to 1000 h. The weight gain during exposure for cured SiMCy is only about 50% of that observed in cured BADCy, suggesting that a significant increase in resistance to water uptake is obtained with the substitution of SiMCy for BADCy. The shape of the curve indicates that changes in solubility, rather than diffusion rate, are primarily responsible for the observed difference, as the kinetics of uptake appear quite similar. To see what effect(s) the water uptake has on mechanical properties, DMTA scans of cured samples of SiMCy were collected both before and after exposure to boiling water for 72 h. The results, shown in Figure 10, indicate that the glass transition temperature (as indicated by the maximum value of the loss modulus) decreases about 40 °C. A similar drop in T<sub>g</sub> has been observed for BADCy after a similar exposure.<sup>1</sup> Note that independent of changes in mechanical properties, the weight gain from absorbed water, as well as the probability of mechanical failure in composite systems due to vaporization of absorbed water on sudden heating, are likely to decrease significantly in composite parts made from SiMCy as compared to BADCy.

\*\*\*\*\* *Insert Figures 9 & 10 here* \*\*\*\*\*

Although it is remotely possible that different impurity sets or concentrations of uncured material might result in a vastly different solubility of water in the cyanate ester systems, the impurities would have to absorb more than their own weight in water. It is highly improbable that the presence of such impurities in a material with a long history of commercial production, in which moisture uptake is a key performance consideration, would have remained unmitigated

such that, by chance, a laboratory synthesis would produce substantially better results. Moreover, the observed moisture uptake of cured BADCy closely matches that reported in previous studies,<sup>37</sup> greatly reducing the chances that the relative performance of the materials is the result of unexpectedly poor performance of the BADCy control. On the other hand, as previously discussed, the solid-state structure of SiMCy in the crystalline state is surprisingly different from that of BADCy, leading to substantially altered intermolecular interactions. Although cured samples are not in a crystalline state, it is reasonable to assume that localized structural correlations extant in the amorphous, cured material would be affected by the same changes in molecular structure that lead to altered crystalline packing. Such alterations in local correlations could alter the degree to which water is absorbed into the cured resin system.

The importance of such a possibility for applications development cannot be understated. With cyanate ester resin set to occupy an important role as state of the art materials in naval and aerospace structures, the uptake of water, in both the unreacted monomer and cured polymer, is a major limitation on performance. The ability to drastically reduce the uptake of moisture by means of a relatively simple change in chemical structure would imply that significantly greater reductions are possible. Although some currently known cyanate ester systems show dramatically reduced uptake of water,<sup>1</sup> these almost always involve changes in chemical structure that also necessitate more difficult processing methods and conditions, or significantly reduced strain to failure. The particularly attractive feature of SiMCy is that moisture uptake is altered with little impact on mechanical properties or cure kinetics. When combined with the superior thermo-oxidative stability displayed by SiMCy, the reduced moisture uptake is a highly encouraging sign that the availability silane-based cyanate esters may represent an important breakthrough in high performance polymer composite resin technology.

**Concluding remarks.** Comparisons between the commercially available BADCy (bisphenol-A based dicyanate ester resin) and an analogous silane-based cyanate ester resin, in which each quaternary carbon atom in the linkage between cyanate ester groups is replaced with a quaternary silicon atom, reveal key differences that make silane-based cyanate esters promising for naval and aerospace applications development. The silane-based resin exhibits improved thermo-oxidative stability even though in an inert atmosphere some thermal stability is lost, suggesting that the presence of silicon could facilitate the development of a silicate-based protective layer in these materials. In addition, the silane-based resin shows significantly lower moisture uptake when exposed to boiling water, which may be due to a difference in the spatial distribution of hydrophilic groups at the molecular scale. Importantly, these improved properties are achieved without significant effects on cure kinetics or basic mechanical properties, meaning that they may be achieved without needing to alter processing methods or substantially redesign structures.

**Acknowledgement.** The authors wish to thank the Office of Naval Research (Code 332) and the American Society for Engineering Education through the Naval Research Laboratory Postdoctoral Fellowship Program for sponsorship of these efforts. The authors also wish to thank Lonza for supplying the BADCy used in this study.

## Experimental

**General Synthetic Methods.** All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Tetrahydrofuran (THF), ether, N-methylpyrrolidinone (99.5%), and dichloromethane solvents were purchased as the anhydrous grade and inhibitor-free from Aldrich and used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were performed using a Bruker AC 200 or Bruker 400 MHz instrument.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported versus the deuterated solvent peak (Solvent,  $^1\text{H}$ ,  $^{13}\text{C}$ :  $\text{CDCl}_3$ ,  $\delta$  7.27 ppm,  $\delta$  77.0 ppm;  $\text{DMSO-d}_6$ ,  $\delta$  2.50 ppm,  $\delta$  39.5 ppm). The dichlorodimethylsilane, p-bromophenol, benzyl chloride, cyanogen bromide (3.0 M in dichloromethane), n-butyllithium (2.5 M in hexanes), and 5% Pd on carbon were purchased from Aldrich Chemical Co. and used as received. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA.

**HPLC Analysis Methods.** For chromatographic analysis, approximately 0.5 mg of each sample was dissolved in 1.5 ml of acetonitrile. Liquid chromatography was carried out using an HPLC system (Shimadzu Corp., Kyoto, Japan) that consisted of a LC-10AD HPLC pump, DGU-14A degasser, SIL-10AD autosampler, and an SPD-M10A diode array detector. Chromatographic separation was carried out on an Econosphere CN 5- $\mu\text{m}$  4.6 X 250 mm HPLC column (Alltech Corp., Deerfield, IL) maintained at 30°C. The pump flow rate was set at 1 mL/min. using an isocratic mobile phase of 45:55 (v/v) acetonitrile:water. The monitoring wavelength was adjusted to 210 nm. The purity was assessed using area percent. The purity of sample BADCy was 98.3% (retention time 4.04 min.) and that of sample SiMCy was 97.0% (retention time 4.15 min.).



**Polymer Characterization Methods.** Differential scanning calorimetry (DSC) was performed on a TA Instruments Q20 Series calorimeter at a heating rate of 10 °C/.min. under 30 cc/min. of flowing nitrogen. Thermogravimetric analysis (TGA) was performed on a TA Instruments 2900 Series Hi-Res thermogravimetric analyzer, also at a heating rate of 10 °C/min., under both flowing nitrogen (60 cc/min.) and flowing air (40 cc/min.). Thermal mechanical analysis (TMA) was conducted using a TA Instruments 2910 thermomechanical analyzer with heating at 10 °C/min. under a nitrogen blanket. Dynamic mechanical thermal analysis (DMTA) was carried out using a Rheometrics Scientific DMTA V in 3-point bending mode, using a heating rate of 20 °C/min up to 150 °C, followed by 10 minutes of equilibration at 150 °C, and subsequent heating at 1 °C/min up to 250 °C, in a nitrogen atmosphere. Fourier Transform Infrared Spectroscopy (FTIR) was performed on a Nicolet 710 infrared spectrophotometer using the average of 128 scans and a resolution of 1 cm<sup>-1</sup>. For DSC and TGA, the fully cured samples were removed from the mold, carefully cleaned, and ground to a fine powder prior to testing. For FTIR samples, the powder was mixed with KBr powder in a pellet press. For TMA, the samples were cut to dimensions of 3 mm x 3 mm, with an as-molded thickness near 1 mm, prior to testing. For DMTA, a flexural specimen of dimensions 43 mm x 10 mm x 3 mm were cast in silicone molds, with de-molding prior to cure at temperatures of 200 °C and above. After cure was complete, the sample was carefully cleaned prior to testing. After the initial test, the sample was placed in boiling water for 72 h, then carefully dried and tested again.

**Preparation of bis(4-benzyloxyphenyl)dimethylsilane (1).** A chilled (-78 °C) THF (200 mL) of 4-bromophenyl benzyl ether (10.00 g, 38.0 mmol, prepared from p-bromophenol, benzyl chloride, and potassium carbonate in DMF) was treated with n-BuLi (15.2 mL, 38 mmol) and allowed to react with stirring for 30 min. This mixture, now heterogeneous, was treated with

dichlorodimethylsilane (2.30 mL, 19 mmol) and the cooling bath removed. The mixture was allowed to react with stirring for an additional 1 h and then diluted with ether (300 mL). The organic layer was washed with water (2 x 200 mL), brine (100 mL), and then dried over MgSO<sub>4</sub>. The mixture was filtered and the solvents removed under reduced pressure to afford **1** as a white solid (8.00 g, ~100%).

**Preparation of bis(4-hydroxyphenyl)dimethylsilane (2).** A THF (150 mL) solution containing **1** (5.00 g, 11.9 mmol) and palladium (5%) on carbon (600 mg) was placed under an atmosphere of hydrogen (~2 psig) and allowed to react with stirring for 24 h. The catalyst was removed by filtration through a plug of Celite and the solvent removed under reduced pressure to afford 2.90 g (~100%) of **2** as light yellow solid. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.25 (d, *J*= 8.4 Hz, 2 H), 6.75 (d, *J*= 8.4 Hz, 2 H), 0.41 (s, 3 H).

**Preparation of bis(4-cyanatophenyl)dimethylsilane (3).** A chilled (-20 °C) ether (50 mL) solution containing **2** (11.0 g, 45.0 mmol) and cyanogen bromide (11.9 g, 113 mmol) was treated with triethylamine (1.8 mL, 13 mmol) in dropwise manner. This mixture was allowed to react for 2 h with stirring at -20 °C. The mixture was filtered to remove the hydrobromide salt and the organic layer was washed with (2 x 150 mL), brine, and then dried over MgSO<sub>4</sub>. The solvents were removed under reduced pressure and crude product crystallized overnight on standing to afford **3** as an off-white solid (mp 58-60 °C, 12.55 g, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.48 (d, *J*= 8.7 Hz, 2 H), 7.21 (d, *J*= 8.7 Hz, 2 H), 0.50 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.9 (*C4*), 136.6 (*C1*), 136.3 (*C2*), 114.9 (*C3*), 108.5 (OCN), -2.5 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Si: C, 65.28; H, 4.79; N, 9.51. Found: C, 65.39; H, 4.89; N, 9.32.

**Water Boil Experiments.** A continuous boiling apparatus was constructed to allow for long-term exposure to water at temperatures in excess of 90 °C. Prior to immersion, the fully

cured samples were placed in a desiccated chamber and weighed periodically to ensure complete dryness. Once dry, the dimensions of the rectangular specimens were recorded along with the dry weight. The dry samples were also photographed prior to immersion. After immersion, the samples were pulled from the boiling water periodically, carefully patted dry, and weighed. The immersion continued until 1000 h of exposure had elapsed, at which point the samples were patted dry and weighed. The final dimensions of the sample were also recorded and a comparative set of photographs obtained.

## References

- [1] Hamerton, I. “*Chemistry and Technology of Cyanate Ester Resins*”, Blackie Academic, Glasgow 1994.
- [2] Fang, T.; Shimp, D. A. *Prog. Polym. Sci.* **1995**, 20, 61.
- [3] Reghunadhan, C. P.; Mathew, D.; Ninan, K. N. *Adv. Polym. Sci.* **2001**, 155, 1.
- [4] Woo, E. M. ; Shimp, D. A.; Seferis, J. C. *Polymer* **1994**, 35, 1658.
- [5] Hwang, J. W.; Cho, K.; Yoon, T. H.; Park, C. E. *J. Appl. Polym. Sci.* **2000**, 77, 921.
- [6] Hwang, J. W. ; Cho, K.; Park, C. E.; Huh, W. *J. Appl. Polym. Sci.* **1999**, 74, 33.
- [7] Chang, J. Y. ; Hong, J. L. *Polymer* **2000**, 41, 4513.
- [8] Chang, J. Y. ; Hong, J. L. *Polymer* **2001**, 42, 1525.
- [9] Takao, I.; Takao, K.; Toshiyuki, O. ; Masao, T. *Polym. Int.* **2003**, 52, 773.
- [10] Harismendy, I. ; Rio, M. D.; Eceiza, A.; Gavalda, J.; Gomez, C. M. ; Mondragon, I. *J. Appl. Polym. Sci.* **2000**, 76, 1037.
- [11] Harismendy, I. ; Rio, M. D.; Marieta, C. ; Gavalda, J. ; Gomez, C. M.; Mondragon, I. *J. Appl. Polym. Sci.* **2001**, 80, 2759.
- [12] Pearson, R. A.; Yee, A. F. *J. Mat. Sci.* **1986**, 21, 2475.
- [13] Bucknall, C. B.; Gilbert, A. H. *Polymer* **1989**, 30, 213.
- [14] Yamanaka, K.; Inoue, T. *Polymer* **1989**, 30, 662.
- [15] Bennett, G. S.; Farris, R. J.; Thompson, S. A. *Polymer* **1991**, 32, 1633.
- [16] Hourston, D. J.; Lane, J. M. *Polymer* **1992**, 33, 1379.
- [17] Ohnaga, T.; Chen, W.; Inoue, T. *Polymer* **1994**, 35, 3774.
- [18] Chen, W. ; Kobayashi, S.; Inoue, T.; Ohnaga, T.; Ougizawa, T. *Polymer* **1994**, 35, 4015.
- [19] Chen, J.-P. ; Lee, Y.-D. *Polymer* **1995**, 36, 55.

- [20] Oyanguren, P. A.; Frontinti, P. M.; Williams, R. J. J. ; Vigier, G.; Pascault, J. P. *Polymer* **1996**, *37*, 3087.
- [21] Elicabe, G. E.; Larrondo, H. A.; Williams, R. J. J. *Macromolecules* **1997**, *30*, 6550.
- [22] Lee, A.; Lichtenhan, J. D. *Macromolecules* **1998**, *31*, 4970.
- [23] Pascault, J. P.; Williams, R. J. in “*Polymer Blends*”, D. R. Paul, C. B. Bucknall, Eds., Vol. 1, 379-415, Wiley, New York 2000, and references therein.
- [24] Bharadwaj, R. K.; Berry, R. J.; Farmer, B. L. *Polymer* **2000**, *41*, 7209.
- [25] Liang, K.; Toghiani, H.; Li, G.; Pittman, C. U. *J. Polym. Sci. Part A, Polym. Chem.* **2005**, *43*, 3887.
- [26] Ganguli, S.; Dean, D.; Jordan, K.; Price, G.; Vaia, R. *Polymer* **2003**, *44*, 1315.
- [27] Le Baron, P.; Wang, Z.; Pinnavaai, T. *Appl. Clay Sci.* **1999**, *15*, 11.
- [28] Islam, M.; Dean, D.; Campbell, S. *Am. Chem. Soc. Polym. Mater.: Sci. Engng.* **2001**, 84.
- [29] Park, S. J.; Jin, F. L.; Lee, J. R. *Macromolecular Research* **2005**, *13*, 8.
- [30] Maya, E. M.; Snow, A. W.; Buckley, L. J. *Macromolecules* **2002**, *35*, 460.
- [31] Wright, M. E. *Am. Chem. Soc., Polym. Preprints* **2004**, *45*, 294.
- [32] Bauer, M.; Bauer, J.; Kuhn, G. *Acta Polym.* **1986**, *37*, 715.
- [33] *Mol-Percent Impurity by Differential Scanning Calorimetry*, ASTM E 928-83.
- [34] A crystallographic report for the structure has been filed with the Cambridge Crystallographic database.
- [35] Fyfe, C. A.; Niu, J.; Rettig, S. J.; Burlinson, N. E.; Reidsema, C. M.; Wang, D. W.; Poliks, M. *Macromolecules* **1992**, *25*, 6289.
- [36] Zheng, L.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2001**, *34*, 8034.
- [37] Shimp, D. A.; Christenson, J. R.; Ising, S. J. *34<sup>th</sup> Int. SAMPE Symp. Exhib.* **1989**, *34*, 222.

## Figure Captions

**Figure 1.** DSC scan of 2,2-cyanatophenylpropane (BADCy) and bis(4-cyanatophenyl)dimethylsilane **3** (SiMCy) near the melting point.

**Figure 2.** HPLC trace of BADCy and bis(4-cyanatophenyl)dimethylsilane **3** (SiMCy).

**Figure 2.** DSC scan of BADCy and SiMCy, (a) on first heating, showing cure of cyanate ester groups, and (b) after the standard cure cycle.

**Figure 4.** FTIR scans of BADCy and SiMCy both just prior to cure (a), and after curing (b).

**Figure 5.** A drawing depicting the molecular structure found in the crystal for *bis*(4-cyanatophenyl)dimethylsilane **3**.(SiMCy)

**Figure 6.** A possible packing interaction in SiMCy shown as a dashed line. Although the distance of 2.84 Å that is just slightly beyond vdW contact (2.65-2.75 for H...N) it does likely represent some kind of weak electrostatic interaction.

**Figure 7.** Another packing interaction in SiMCy. The short contact is 2.62 Å and that is slightly less than van der Waals, so it can be assigned as a weak H-bond. This interaction proliferates to link the molecules together in an infinite not-quite-planar ribbon.

**Figure 8.** TGA weight loss and rate plots of cured BADCy and cured SiMCy (a) under nitrogen atmosphere, and (b) in air

**Figure 9.** Weight gain of samples of cured BADCy and cured SiMCy during exposure to boiling water.

**Figure 10.** DMTA scan of cured SiMCy both (a) before and (b) after 72 h exposure to boiling water.

**Table 1.** Summary of crystal data and structure refinement for **3**.

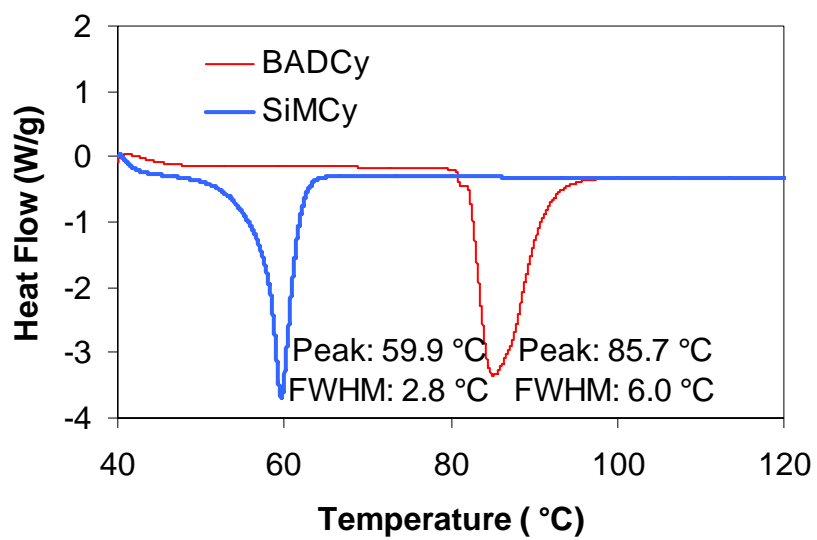
Empirical formula	$C_{16} H_{14} N_2 O_2 Si$	
Formula weight	294.38	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 16.6524(14) \text{ Å}$	$\alpha = 90^\circ$ .
	$b = 12.6161(10) \text{ Å}$	$\beta = 97.417(2)^\circ$ .
	$c = 7.4520(6) \text{ Å}$	$\gamma = 90^\circ$ .
Volume	$1552.5(2) \text{ Å}^3$	
Z	4	
Density (calculated)	$1.259 \text{ Mg/m}^3$	
Absorption coefficient	$0.156 \text{ mm}^{-1}$	
F(000)	616	
Crystal size	$0.52 \times 0.24 \times 0.18 \text{ mm}^3$	
Theta range for data collection	$1.23$ to $26.37^\circ$ .	
Index ranges	$-20 \leq h \leq 20$ , $-15 \leq k \leq 15$ , $-8 \leq l \leq 9$	
Reflections collected	12529	
Reflections 'observed'	2447 [ $I > 2\sigma(I)$ ]	
Independent reflections	3176 [ $R(\text{int}) = 0.0370$ ]	
Completeness to $\theta = 26.37^\circ$	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.977 and 0.693	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	3176 / 0 / 192	
Goodness-of-fit on $F^2$	1.036	
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0406$ , $wR2 = 0.1086$	
R indices (all data)	$R1 = 0.0556$ , $wR2 = 0.1182$	
Largest diff. peak and hole	$0.370$ and $-0.180 \text{ e.Å}^{-3}$	

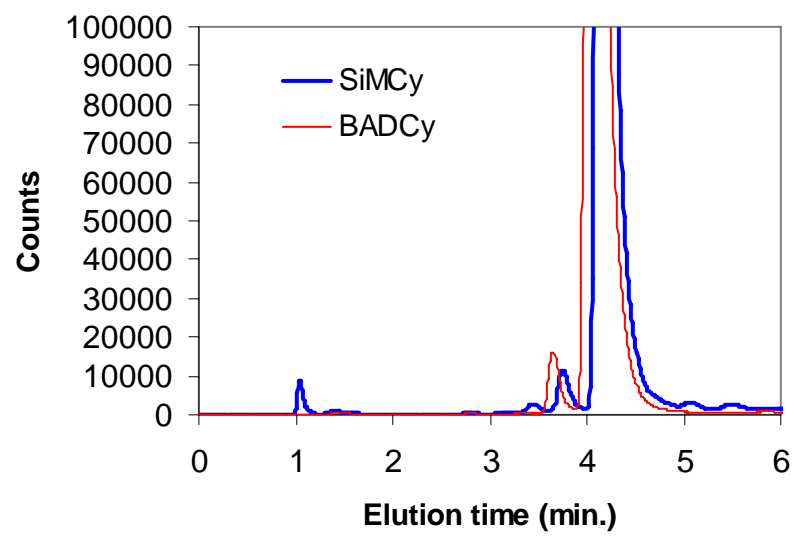


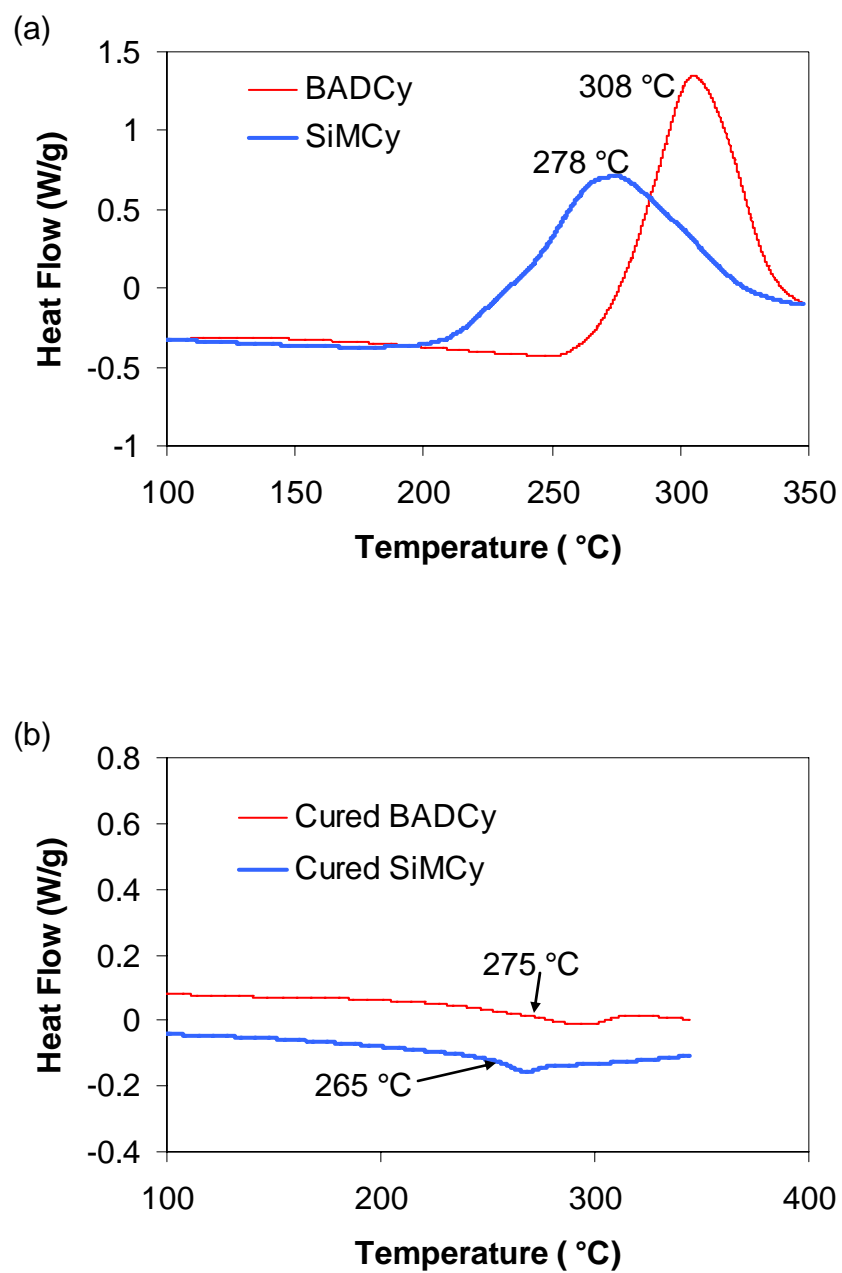
**Table 2.** Mechanical properties of cured SiMCy and BADCy.

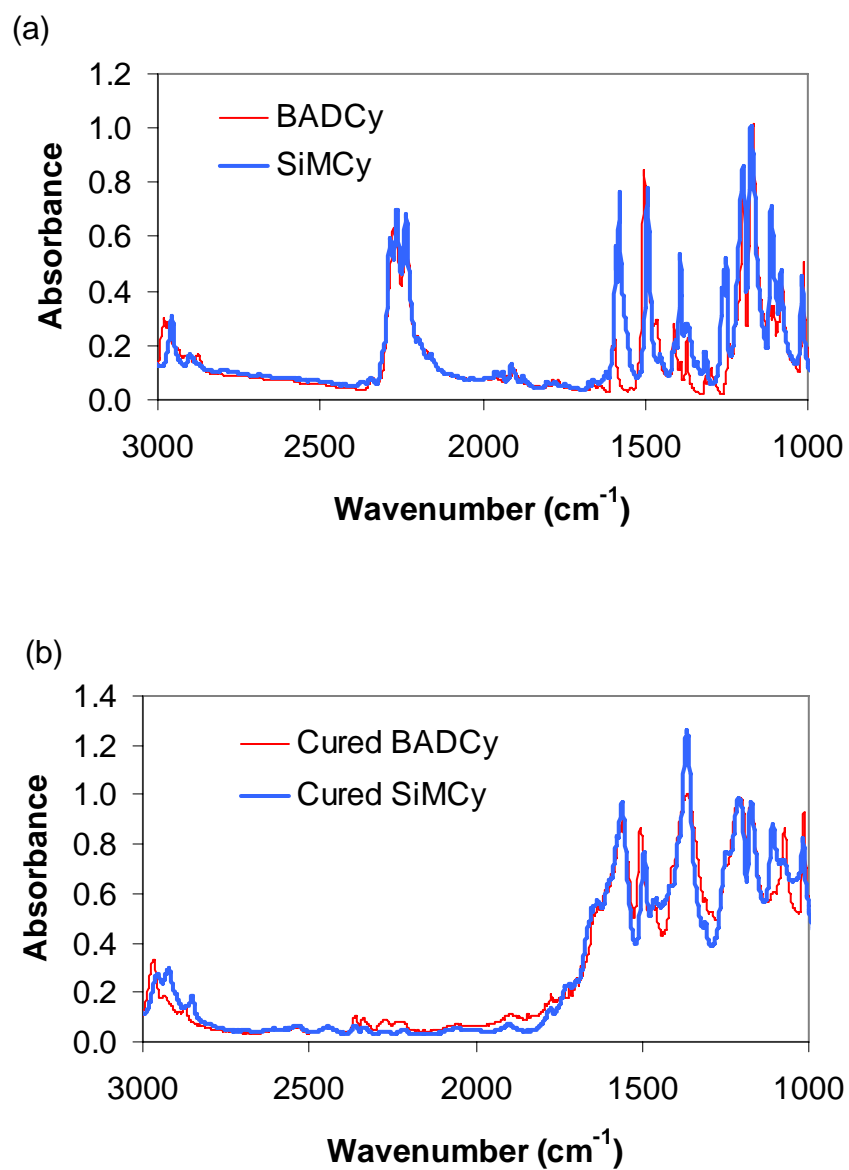
Property	Unit	SiMCy		BADCy	
		Value	Std. Dev..	Value	Std. Dev.
Unnotched Izod Impact Strength	J/m	38	±3	39	±2
Tensile Modulus	MPa	2800	n/a	3100*	n/a
Strain to Failure in Tension	%	3	n/a	3.2*	n/a
Coefficient of Thermal Expansion	μm/m °C	93	±4	50	±4

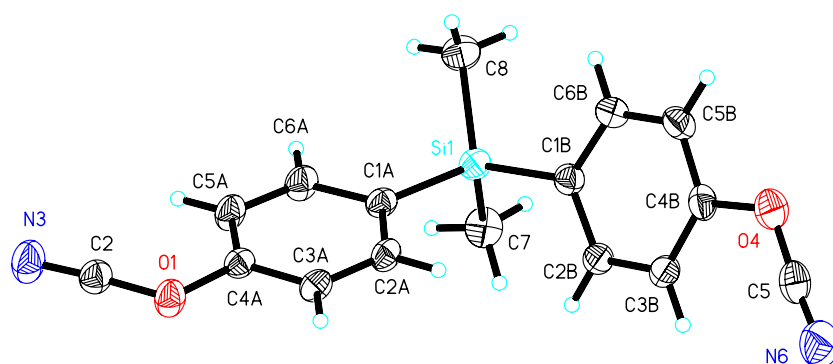
\* data reported in ref 1,

**Figure 1**

**Figure 2**

**Figure 3**

**Figure 4**

**Figure 5**

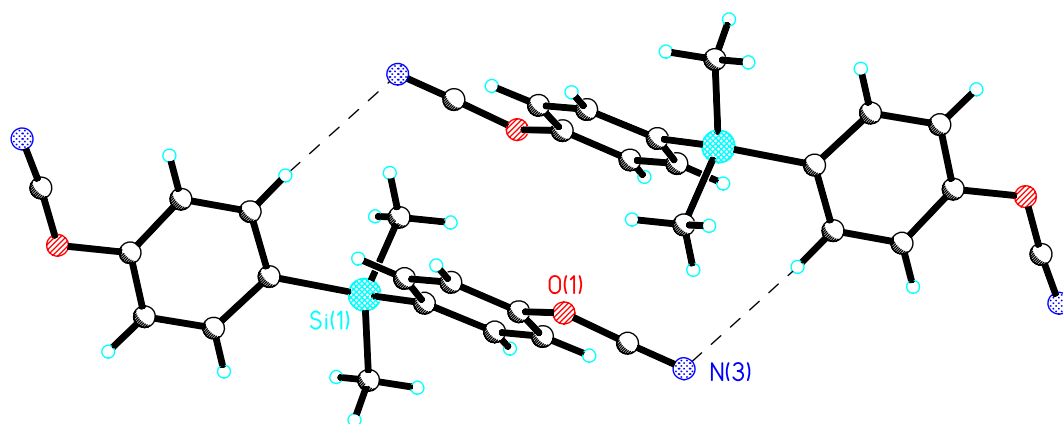
**Figure 6**

Figure 7

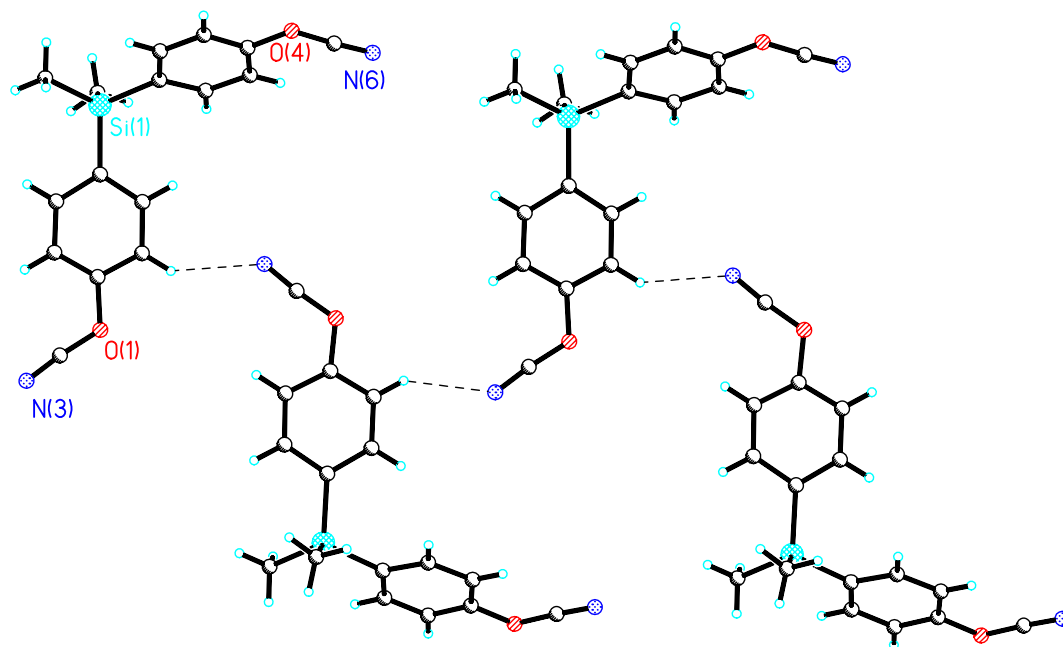
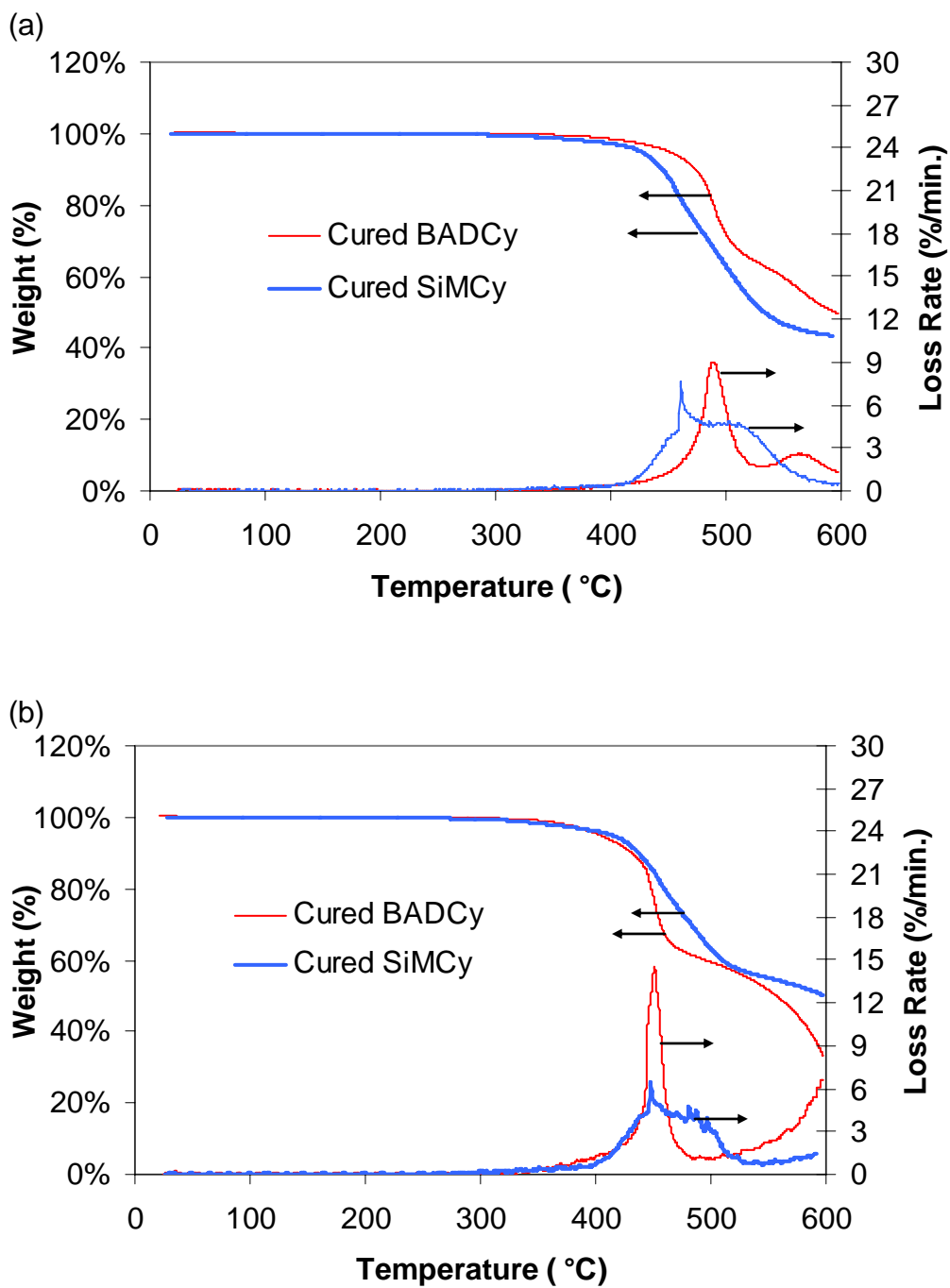




Figure 8



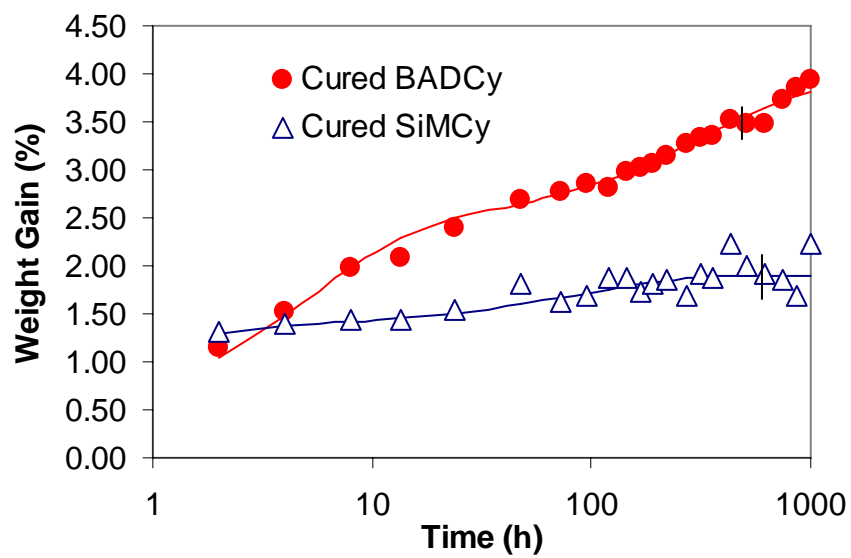
**Figure 9**

Figure 10

